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(54) Nickel positive electrode for use in alkaline storage battery and nickel-hydrogen storage
battery using the same

In alkalischer Speicherbatterie verwendete positive Nickelelektrode und diese Elektrode verwendende
Nickel-Wasserstoff Speicherbatterie

Electrode positive de nickel utilisée dans une pile de stockage alcaline et pile de stockage
nickel-hydrogène utilisant cet électrode

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Description**BACKGROUND OF THE INVENTION****5 Field of the Invention**

The present invention relates to a nickel positive electrode having improved characteristics for use in alkaline storage batteries using the positive electrodes of nickel oxide and the negative electrodes of a hydrogen storage alloy capable of electrochemically absorbing and desorbing hydrogen, cadmium, or zinc, to an alkaline storage battery containing such a nickel positive electrode and to a nickel-hydrogen storage battery having improved characteristics.

10 Description of the Related Art

Recently, there has been an intensive need for high energy density secondary batteries associated with portable appliances which are made much more valuable, compact and lighter in weight. Similarly, such new high energy density secondary cells are also vigorously sought for power supplies for electric automobiles. To cope with these needs, in the technical field of nickel-cadmium cell (referred to as Ni/Cd cell hereunder), there have been developed a Ni/Cd cell having a higher capacity using conventional sintered nickel positive electrodes and further a much higher energy density Ni/Cd cell having a capacity of 30 to 60 % greater than that of the former using foamed metal type nickel positive electrodes. Moreover, there has been developed a nickel-hydrogen storage battery with negative electrodes of a hydrogen storage alloy having a higher capacity than those of Ni/Cd cells, i.e., a capacity two times or more as great as those of Ni/Cd cells using sintered nickel positive electrodes. These high capacity alkaline storage batteries include positive electrodes composed of a sintered porous nickel body, a bulk foamed porous nickel body, or a porous fibrous nickel body of a high porosity (90 % or more) which are filled with nickel hydroxide powder to a high density in order to achieve an improvement in energy density of the positive electrodes. Consequently, modern sintered nickel positive electrodes have an improved energy density of 450 to 500 mAh/cm³, and foamed metal type nickel positive electrodes have an energy density of 550 to 650 mAh/cm³, as opposed to conventional sintered nickel positive electrodes having an energy density of 400 to 500 mAh/cm³. Those positive electrodes composed of a sintered porous nickel body, a foamed porous nickel body, or a porous fibrous nickel body which are filled with nickel hydroxide powder to a high density have a problem that their energy density can be maintained at higher levels about at normal temperature, but reduced at high temperature atmosphere. Therefore, it is difficult to take advantages of the characteristics of high energy density in a wider temperature range. This is attributed to the fact that a charge reaction accompanied by a conversion from nickel hydroxide to nickel oxyhydroxide and an oxygen evolving reaction are liable to simultaneously occur under a high temperature atmosphere. That is, an oxygen evolving overvoltage at positive electrodes is reduced leading to an insufficient charge reaction of the conversion of nickel hydroxide to nickel oxyhydroxide with a reduced rate of utilization of the nickel hydroxide. In order to overcome this problem, the following methods have been proposed:

- (1) a method where cadmium oxide powder or cadmium hydroxide powder is added into positive electrodes, and
- (2) a method where cadmium oxide is incorporated into the nickel hydroxide powder (Japanese Patent KOKAI (Laid-open) No. 61-104565).

In the conventionally proposed methods (1) and (2) as above, the presence of cadmium oxide inside or with the nickel hydroxide powder improves the rate of utilization of the nickel hydroxide under a high temperature atmosphere. However, even when the addition of cadmium oxide is made, the rate of utilization of the nickel hydroxide under a high temperature atmosphere is only on the order of 80 %. In order to improve the rate of utilization of the nickel hydroxide under a high temperature atmosphere, the amount of cadmium oxide to be added into inside the nickel hydroxide or into the nickel positive electrodes must be increased. However, the increase of the amount of cadmium oxide to be added causes a problem of adversely diminishing the rate of utilization of the nickel hydroxide about at normal temperature though the rate of utilization of the nickel hydroxide under a high temperature atmosphere may be improved up to about 90 %.

In recent years, attention has been directed to a nickel-hydrogen storage battery containing no cadmium, heavy metal, from the point of environmental hazards. The removal of cadmium oxide from the nickel hydroxide or the positive electrodes, however, produces problems that the rate of utilization of the nickel hydroxide under a high temperature atmosphere is reduced to on the order to 50 to 60 % and that when a sealed nickel-hydrogen storage battery with a positive electrode capacity controlled is arranged under less electrolyte conditions, the cycle life is shortened. The present invention is to overcome these problems by providing a nickel positive electrode for use in alkaline storage batteries having an excellent rate of utilization of the nickel hydroxide in an atmosphere in a wide range of temperature. Moreover, an object of the present invention is to provide a nickel-hydrogen storage battery being excellent in the cell

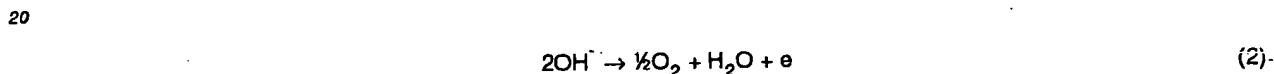
capacity and in the cycle life in an atmosphere in a wide range of temperature.

US-A-3,826,684 discloses to add compounds of magnesium, calcium, strontium and barium to a paste for the production of positive nickel electrodes.

JP-A-63-045 754 discloses the addition of barium hydroxide to an active material in a storage battery, the amount of barium hydroxide being limited to a range of from 0.5 to 5.0 mol%. Thereby, a decrease in discharge voltage can be prevented.

According to the invention, there is provided a paste type nickel positive electrode for use in alkaline storage batteries according to Claim 1, an alkaline storage battery containing such a nickel positive electrode and a nickel-hydrogen storage battery according to Claim 13, respectively. Preferred embodiments of the invention are claimed in the subclaims.

The inclusion of at least one of compounds of yttrium, indium, antimony, barium and beryllium into the nickel positive electrode (2) allows these compounds to be absorbed on the surfaces of the active material, the nickel oxide resulting in an increase in the overvoltage of evolving oxygen due to a competitive reaction (2) at charging under a high temperature atmosphere. As a result, the charge reaction of the conversion of the nickel hydroxide to nickel oxyhydroxide according to the equation (1) is sufficiently effected with an improvement in the rate of utilization under a high temperature atmosphere.



Moreover, the incorporation of a calcium compound into the paste type nickel positive electrode containing cobalt a synergistic effect of the cobalt and the calcium compound result in an increase in the overvoltage of evolving oxygen due to the competitive reaction at charging under a high temperature atmosphere with an improvement in the rate of utilization under high temperature atmosphere for the nickel positive electrode owing to the same effect as described above. When these compounds are added in an appropriate amount, they do not affect on the rate of utilization of the nickel hydroxide. Therefore, the inclusion of the compounds according to the present invention permits the attainment of a positive electrode being excellent in the rate of utilization of the active material in a wide range of temperature. For practical nickel-hydrogen storage batteries, the charging efficiency according to the above equation (1) may be enhanced by adding cobalt and the calcium compounds to the positive electrode so as to have a specific gravity of 1.2 to 1.3, thereby achieving an excellent discharge capacity in a wide temperature range. Moreover, under the conditions that at least one of calcium compounds and zinc oxide or zinc hydroxide is incorporated in the positive electrode and that the specific gravity and the amount of the alkaline electrolyte range from 1.2 to 1.3 and from 1.0 to 2.5 cm³/Ah, respectively, and that the negative capacity is not less than 1.1 times the positive electrode capacity, localized presence and leakage of the electrolyte inside the cells owing to the repetition of a charge-discharge cycle are inhibited so that the cycle life is improved. These results are recognized to be attributed to the synergistic effect of the conditions of cell design such as the specific gravity and the amount of the electrolyte and the ratio of the negative electrode capacity to the positive electrode capacity and the mixture of at least one of zinc oxide or zinc hydroxide and calcium compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of the nickel-hydrogen storage battery structured according to the present invention.

In Figure 1, 1 designates a negative electrode, 2 does a positive electrode, 3 does a separator, 4 does a case, 6 is a relief valve, and 7 does a seal plate.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

The present invention is illustrated with reference to Examples herein under.

Example 1

Nickel-hydrogen storage batteries were manufactured in the following way, using constituents as shown in table 1 as powders. Ni(OH)_2 was used in the form of spherical nickel hydroxide powder.

To each mixture there was added water to form a paste which was filled into a porous support of foamed nickel

having a porosity of 95 % and a facial density of 300 g/cm², dried, pressed, and thereafter, immersed in an aqueous dispersion of fluorinated resin powder. Thereafter, the impregnated support was redried and cut into predetermined dimensions to produce various nickel positive electrodes having a theoretical capacity of 1000 mAh.

5 Next, the positive electrode 2 produced as above and a hydrogen storage alloy negative electrode 1 (the hydrogen storage alloy had a composition of $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$) were rolled in a spiral form with a separator being interposed therebetween, and inserted in a case 4 which also acts as a negative terminal. Thereafter, in the resultant assembly, there were injected 2.0 cm^3 of an alkaline electrolyte which was a solution of lithium hydroxide dissolved in an aqueous solution of potassium hydroxide having a concentration of 20 g/l and having a specific gravity of 1.3, followed by sealing the case 4 with a seal plate 7 equipped with a relief valve 6 to constitute a sealed nickel-hydrogen storage battery of a AA size having a theoretical capacity of 1000 mAh with the cell capacity being controlled by the positive electrode. The arrangement of the resultant battery is shown in Figure 1, in which 8 designates an insulating gasket, and 9 designates a positive current collector electrically connecting the positive electrode 2 and the seal plate 7. In this way, various cells were made using positive electrodes and evaluated for the rate of utilization of the positive electrode. The cells were charged at a charge rate of 0.1 C for 15 hours at a temperature of $20, 30, 40$ and 50°C in ambient atmosphere, and then left to stand for three hours at 20°C in ambient atmosphere, and thereafter, discharged at a discharge rate of 0.2 C in ambient atmosphere at 20°C until reaching 1.0 V . After performing the charge and discharge cycles under the aforementioned conditions, the rate of utilization of the positive active material, nickel hydroxide, was determined by calculation according to the following equation:

20 Rate of utilization of positive electrode (%) = (Discharge capacity/1000 mAh) × 100

25 Although description has been made for the amount of calcium added in a ratio by weight of 3 in this Example, the amount of calcium in the ratio ranging from 0.5 to 5 by weight gives rise to good results similarly to the case in Example 1. Moreover, although a foamed nickel having a nominal weight of 300 g/m² has been used for supports to retain the positive electrode active materials, those having a nominal weight ranging from 200 to 700 g/cm² are preferred from the point of view of energy density. Furthermore, the identical effects could be obtained even by using other supports such as a porous fibrous nickel body, a sintered porous nickel body, punched metal, expanded metal, nets, or foils. Similarly, other cells or batteries such as Ni/Cd cells, nickel-zinc storage batteries, and the like other than the nickel-hydrogen storage batteries can attain the same effects so long as they are of such type as using the nickel positive electrode. In this Example, description has been made for the use of nickel hydroxide, cobalt and calcium compounds, though zinc oxide and zinc hydroxide may be further added to achieve an additional improvement in the rate of utilization under high temperature atmosphere.

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Table 3
Constituents of various cells (* - Comparison Examples)

Cell No.	Positive electrode composition (Weight ratio)					Electrolyte S.G.	Amount (cm ³ / Ah)	Capacity ratio Negative electrode/ Positive electrode
	Ni(OH) ₂	Co	Co(OH) ₂	ZnO	Ca(OH) ₂			
* 1	100	5	5					
* 2	100	5	5	3				
* 3	100	5	5		3			
4	100	5	5	3				
5	100	5	5	2	1			
* 6	100	5	5	0.2		3	1.3	2.0
7	100	5	5	0.5		3		
8	100	5	5	1		3		
9	100	5	5	5		3		
* 10	100	5	5	6		3		
* 11	100	5	5	3		0.2		
12	100	5	5	3		0.5		

Table 3 (continued)

Cell No.	Positive electrode composition (Weight ratio)					S.G.	Electrolyte Amount (cm ³ /Ah)	Capacity ratio Negative electrode/ Positive electrode
	Ni(OH) ₂	Co	Co(OH) ₂	ZnO	Zn(OH) ₂			
13	100	5	5	3		1		
14	100	5	5	3		5	1.3	
* 15	100	5	5	3		6	2.0	1.5
16							1.15	
17							1.20	
18							2.0	1.5
19							1.35	
20	100	7	5	2		3	1.30	
21							1.0	0.95
22							2.5	
23							3.0	
24							1.30	2.0
								1.0
								1.1

The cell capacity was controlled by the positive electrodes with the theoretical capacity being 1000 mAh. For a separator, there was used sulfonated polypropylene non-woven fabric, i.e., a sulfonated separator. These cells were

evaluated for discharge capacity in ambient atmosphere at temperatures of 20, 40 and 50 °C. The discharge capacity was determined by charging the cells at a charge rate of 0.1 C for 15 hours in ambient atmosphere at a temperature of 20, 40 and 50 °C, and then left to stand for three hours in an atmosphere at 20 °C, and thereafter, discharged at a discharge rate corresponding to 0.2 C in an atmosphere at 20 °C until reaching 1.0 V. The cycle life was determined by charging the cells at 1 C for 1.3 hours and then discharging at 1C until 1.0 V is reached, in ambient atmosphere at a temperature of 0, 20, 40 °C, and repeating this charge and discharge cycle until a deterioration of 40 % based on the initial discharge capacity is attained, which time was taken as the end of the working life. Cells Nos. 1, 2, 3, 4 and 5 were evaluated for cell capacity and cycle life, the results of which are given in Table 4.

Table 4

Discharge capacities and cycle lives of various cells						
Cell No.	Discharge capacity (mAh)			Cycle life / ∞		
	20 °C	40 °C	50 °C	0 °C	20 °C	40 °C
*1	970	580	350	150	250	250
*2	970	610	350	350	450	453
*3	950	850	780	250	370	360
4	950	865	775	460	530	510
5	950	860	770	460	539	515

(* = Comparison Examples)

In the Table 4, it can be seen that Cell No. 1 is inferior in the discharge capacity at 40 °C and 50 °C and in the cycle life in the temperature range of 0 to 40 °C because of containing no zinc oxide nor calcium hydroxide in the positive electrode. Cell No. 2 containing zinc oxide in the positive electrode is considerably improved in the cycle life over Cell No. 1, though it is little improved in the discharge capacity at 40 °C and 50 °C. Cell No. 3 containing calcium hydroxide is improved in the discharge capacity at 40 °C and 50 °C over Cells Nos. 1 and 2, though it is only a little improved in the cycle life over Cell No. 1. As above, Cells Nos. 1, 2 and 3 are lacking in an overall balance among cell characteristics even though they are constituted in an ideal state with respect to the specific gravity and the amount of the electrolyte and the ratio in capacity of the negative electrode to the positive one. In contrast, it can be seen that Cells Nos. 5 and 4 containing cobalt, cobalt hydroxide, zinc oxide, zinc hydroxide and calcium hydroxide in the positive electrode are excellent in the discharge capacity at 20 to 50 °C and the cycle life in the range of 0 to 40 °C. The improvements in discharge capacity and cycle life may be attributed to the synergistic effect of cobalt, zinc and calcium.

Next, Cells Nos. 6, 7, 8, 9, 10 were evaluated for discharge capacity and cycle life in the same procedure as above, the results of which are given in Table 5.

Table 5

Discharge capacities and cycle lives of various cells						
Cell No.	Discharge capacity (mAh)			Cycle life / ∞		
	20 °C	40 °C	50 °C	0 °C	20 °C	40 °C
*6	970	845	780	150	250	250
7	970	843	782	350	450	453
8	950	850	780	390	450	453
9	915	865	775	460	530	510
*10	850	860	772	470	530	500

(* = Comparison Examples)

It is evident from Table 5 that Cell No. 6 has poor cycle life owing to the amount of zinc oxide added being in a weight ratio of 0.2 and that Cell No. 10 has poor discharge capacity at 20 °C owing to the amount of zinc oxide added being in a weight ratio of 6. From these results, the optimum amount of zinc oxide to be added is in a weight ratio ranging 0.5 to 5.

Table 6

Discharge capacities and cycle lives of various cells						
Cell No.	Discharge capacity (mAh)			Cycle life / ∞		
	20 °C	40 °C	50 °C	0 °C	20 °C	40 °C
*11	970	610	400	450	440	450
12	970	715	600	450	450	453
13	950	790	700	460	450	453
14	915	900	780	460	530	510
*15	850	890	772	370	430	460

(* = Comparison Examples)

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It can be seen clearly from the results of Table 6 that Cell No. 11 containing calcium hydroxide added in a weight ratio of 0.2 has poor discharge capacity at 40 °C and 50 °C and that Cell No. 11 is inferior in the discharge capacity at 20 °C and in the cycle life at 0 °C due to the amount of calcium hydroxide added being in a weight ratio of 6. From the foregoing, the amount of calcium hydroxide to be added should be preferably in a weight ratio ranging from 0.5 to 5 as in Cells Nos. 12 to 14. This additive alone is difficult to act effectively, but it can improve the overall cell characteristics in the presence of cobalt, cobalt hydroxide, zinc oxide and calcium hydroxide.

Next, Cells Nos. 16 to 24 were evaluated for cell characteristics, the results of which are summarized in Table 7.

Table 7

Discharge capacities and cycle lives of various cells						
Cell No.	Discharge capacity (mAh)			Cycle life / ∞		
	20 °C	40 °C	50 °C	0 °C	20 °C	40 °C
16	860	850	700	460	530	510
17	930	860	750	460	530	510
18	950	855	770	320	400	350
19	820	730	610	150	180	170
20	930	830	750	400	490	470
21	950	870	780	480	550	530
22	950	870	780	200	350	300
23	950	770	650	200	310	250
24	950	865	775	430	502	409

As shown in Table 7, Cell No. 16 has a reduced discharge capacity of 860 mAh at 20 °C due to the specific gravity of the electrolyte being 1.15. Cell No. 18 has a reduced cycle life due to the specific gravity of the electrolyte being 1.35. From the results of Cells Nos. 4 and 5 in Table 4 and Cell No. 17 in Table 7, the specific gravity of the electrolyte should be preferably in the range of 1.2 to 1.3. The following Cells Nos. 19 to 22 were evaluated for the effects of the amount of the electrolyte, from the results of which the amount of the electrolyte should be preferably in the range of 1.0 to 2.5 cm³/Ah as shown in the results of Cells Nos. 20 and 21. Cell No. 19 containing less amount of the electrolyte is lowered both in the cycle life and the discharge capacity because of an insufficient reaction at electrodes. When the paste type nickel positive electrodes are used, the cobalt, zinc and calcium included in the positive electrodes react with the electrolyte so that the electrolyte has a lower specific gravity. In case less amount of the electrolyte is present, the discharge capacity and the cycle life are diminished. Cell No. 22 containing a larger amount of the electrolyte underwent a leakage of the electrolyte at the time of overcharging because an insufficient gas absorption reaction occurred in the cell resulting in a reduction in cycle life. Next, the examination on the correlation between the ratio of the negative electrode capacity to the positive one and the cell characteristics indicated that a proportion of 1.0 diminished the cycle life and the discharge capacity at a temperature not lower than 40 °C as shown in Cell No. 23. This diminishing of the cycle life may be caused by the suppression of oxygen gas evolution at charging with the negative electrode

being sufficiently charged due to the addition of cobalt, zinc and calcium to the positive electrode, so that the ratio of 1.0 causes insufficient gas absorbing ability in the negative electrode resulting in the leakage of the electrolyte. The diminishing of the discharge capacity at a temperature not lower than 40 °C may be attributed to a decrease in the charging efficiency of the negative electrode rather than the positive electrode so that the discharge capacity of the cell is restricted at the negative electrode. Therefore, the ratio of the negative electrode capacity to the positive one must be at least 1.1 or more as shown in Cell No. 24.

Although calcium hydroxide was used in this Example, the identical results can be obtained by using other calcium compounds such as calcium oxide, calcium sulfide, calcium peroxide and calcium silicate. Similar results can be also obtained by using an alkaline electrolyte comprising at least one of sodium hydroxide and potassium hydroxide, and lithium hydroxide so long as the specific gravity and the amount are appropriate. Although description has been made for the cylindrical sealed nickel-hydrogen storage battery in the present Examples, the identical effects can be attained for a square type or a large capacity type of nickel-hydrogen storage battery as used for electric automobiles.

The present invention provides a paste type nickel positive electrode comprising a major component of nickel oxide and a bulk porous body, porous plate, or plate supporting the nickel oxide and imparting electroconductivity thereto, where the positive electrode contains at least one of cobalt, cobalt hydroxide and cobalt oxide and at least one of calcium compounds incorporated therein. In still another aspect, the present invention provides a nickel-hydrogen storage battery comprising a nickel positive electrode composed of a major component of nickel oxide, a negative electrode consisting of a main body composed of an hydrogen storage alloy capable of electrochemically absorbing and desorbing hydrogen, an alkaline electrolyte, a separator, a case surrounding them, and sealing plate equipped with a relief valve, where the nickel positive electrode before initial charge is of a paste type and contains in the powdery form nickel hydroxide, at least one of cobalt, cobalt hydroxide and cobalt oxide, at least one of zinc oxide and zinc hydroxide and a calcium compound, said at least one of zinc oxide and zinc hydroxide being 0.5 to 5 parts by weight, said calcium compound being 0.5 to 5 parts by weight based on 100 parts by weight of the nickel hydroxide, and a bulk porous body or plate supporting said powdery components and imparting electroconductivity thereto, said alkaline electrolyte having a specific gravity of 1.2 to 1.3 (20 °C), the theoretical negative electrode capacity being not less than 1.1 times the theoretical positive electrode capacity, and the amount of electrolyte being 1.0 to 2.5 cm³/Ah cell capacity. By employing a simple constitution as above, there can be provided a positive electrode for use in alkaline storage batteries which is excellent in the rate of utilization of the nickel hydroxide in ambient atmosphere in a wide range of temperature. Moreover, there can be provided a nickel-hydrogen storage battery which has an excellent cell capacity in an atmosphere in a wide temperature range and an excellent cycle life.

Claims

35. 1. A paste type nickel positive electrode for use in alkaline storage batteries comprising an active material containing a major component of nickel oxide and a support selected from the group consisting of a bulk porous body, porous plate and a plate supporting said active material and imparting electroconductivity thereto, wherein said active material contains at least one selected from the group consisting of cobalt, cobalt hydroxide and cobalt oxide, at least one of calcium compounds and at least one selected from the group consisting of zinc oxide and zinc hydroxide, wherein said calcium compound and said zinc compound are each included in an amount of 0.5 to 5 parts by weight based on 100 parts by weight of said nickel oxide.
40. 2. The nickel positive electrode for use in alkaline storage batteries according to Claim 1, wherein said calcium compound is one selected from the group consisting of calcium oxide, calcium hydroxide, calcium fluoride, calcium-sulfide, calcium peroxide and calcium silicate.
45. 3. The nickel positive electrode for use in alkaline storage batteries according to Claim 1 or 2, wherein said active material is of a paste type.
50. 4. The nickel positive electrode for use in alkaline storage batteries according to Claim 3, wherein said active material contains at least one selected from the group consisting of carbon and nickel.
55. 5. The nickel positive electrode for use in alkaline storage batteries according to any preceding claim, wherein said bulk porous body is one selected from the group consisting of foamed porous nickel body, fibrous porous nickel body, sintered porous nickel body, porous plate, perforated metal and expanded metal.
60. 6. The nickel positive electrode for use in alkaline storage batteries according to any preceding claim, wherein said plate is a nickel or nickel plated iron foil.

7. The nickel positive electrode for use in alkaline storage batteries according to Claim 5 or 6, wherein said foamed porous nickel body and said fibrous porous nickel body have a facial density of 200 to 700 g/m².

5 8. The nickel positive electrode for use in alkaline storage batteries according to any preceding claim, wherein said active material contains at least one selected from the group consisting of compounds of yttrium, indium, antimony, barium and beryllium.

10 9. The nickel positive electrode for use in alkaline storage batteries according to Claim 8, wherein said compounds of yttrium, indium, antimony, barium and beryllium are Y₂O₃, Y(OH)₃, In₂O₃, In₂O, In₂O₃·H₂O, Sb₂O₃, Sb₂O₄, Ba(OH)₂, BeO and Be(OH)₂.

15 10. The nickel positive electrode for use in alkaline storage batteries according to Claim 8 or 9, wherein said compounds of yttrium, indium, antimony, barium and beryllium are included in an amount of 0.5 to 5 parts by weight based on 100 parts by weight of said nickel oxide.

15 11. The nickel positive electrode for use in alkaline storage batteries according to any preceding claim, wherein said nickel oxide is like spherical nickel hydroxide particles.

20 12. An alkaline storage battery containing a nickel positive electrode according to any preceding claim.

20 13. A nickel-hydrogen storage battery which comprises a nickel positive electrode comprising an active material containing a major component of nickel oxide, a negative electrode consisting of a main body composed of a hydrogen storage alloy capable of electrochemically absorbing and desorbing hydrogen, an alkaline electrolyte, a separator, a case surrounding those cell components, and sealing plate equipped with relief valve, wherein:

25 said nickel positive electrode before initially charging comprises nickel hydroxide, at least one of cobalt, cobalt hydroxide and cobalt oxide, at least one of zinc oxide and zinc hydroxide and at least one of calcium compounds in a paste, said at least one of zinc oxide and zinc hydroxide being 0.5 to 5 parts by weight, said at least one of calcium compounds being 0.5 to 5 parts by weight based on 100 parts by weight of the nickel hydroxide;

30 a bulk porous body, porous plate, or plate supporting said paste and imparting electroconductivity thereto; said alkaline electrolyte having a specific gravity of 1.2 to 1.3 at 20 °C;

35 the theoretical negative electrode capacity being not less than 1.1 times the theoretical positive electrode capacity; and

the amount of electrolyte being 1.0 to 2.5 cm³/Ah cell capacity.

40 14. The nickel-hydrogen storage battery according to Claim 13, wherein said calcium compound is one selected from the group consisting of calcium oxide, calcium hydroxide, calcium fluoride, calcium sulfide, calcium peroxide and calcium silicate.

45 15. The nickel-hydrogen storage battery according to Claim 13 or 14, wherein said bulk porous body is one selected from the group consisting of foamed porous nickel body, fibrous porous nickel body, sintered porous nickel body, porous plate, perforated metal and expanded metal.

50 16. The nickel-hydrogen storage battery according to any of Claims 13 to 15, wherein said plate is a nickel or nickel plated iron foil.

55 17. The nickel-hydrogen storage battery according to Claim 15 or 16, wherein said foamed porous nickel body and said fibrous porous nickel body have a facial density of 200 to 700 g/m².

18. The nickel-hydrogen storage battery according to any of Claims 13 to 17, wherein said alkaline electrolyte comprises at least one of potassium hydroxide and sodium hydroxide, and lithium hydroxide.

55 19. The nickel-hydrogen storage battery according to any of Claims 13 to 18, wherein said separator is sulfonated.

20. The nickel-hydrogen storage battery according to any of Claims 13 to 19, wherein said nickel positive electrode contains at least one selected from the group consisting of carbon and nickel.

5 Patentansprüche

1. Positive Nickelektrode vom Pastentyp zur Verwendung in alkalischen Speicherbatterien, aufweisend ein aktives Material, welches einen Hauptbestandteil aus Nickeloxid und einen Träger enthält, der aus der Gruppe ausgewählt ist, die aus einem voluminösen porösen Körper, einer voluminösen porösen Platte und einer voluminösen Platte besteht, welche das aktive Material trägt und diesem eine elektrische Leitfähigkeit vermittelt, wobei das aktive Material mindestens eines enthält, das aus der Gruppe ausgewählt ist, die aus Kobalt, Kobalthydroxid und Kobaltoxid besteht, mindestens eine von Calciumverbindungen und mindestens eines, das aus der Gruppe ausgewählt ist, die aus Zinkoxid und Zinkhydroxid besteht, wobei die Calciumverbindung und die Zinkverbindung jeweils in einer Menge von 0,5 bis 5 Gewichtsteilen basierend auf 100 Gewichtsteilen des Nickeloxids enthalten sind.
2. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach Anspruch 1, wobei die Calciumverbindung eine ist, die aus der Gruppe ausgewählt ist, welche aus Calciumoxid, Calciumhydroxid, Calciumfluorid, Calciumsulfid, Calciumperoxid und Calciumsilicat besteht.
3. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach Anspruch 1 oder 2, wobei das aktive Material vom Pastentyp ist.
4. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach Anspruch 3, wobei das aktive Material mindestens eines enthält, welches aus der Gruppe, die aus Kohlenstoff und Nickel besteht, ausgewählt ist.
5. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach einem der vorstehenden Ansprüche, wobei der voluminöse poröse Körper einer ist, der aus der Gruppe ausgewählt ist, die aus einem geschäumten porösen Nickelkörper, einem faserartigen porösen Nickelkörper, einem gesinterten porösen Nickelkörper, einer porösen Platte, einem perforierten Metall und einem expandierten Metall besteht.
6. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach einem der vorstehenden Ansprüche, wobei die Platte eine Nickelfolie oder einenickelplatierte Eisenfolie ist.
7. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach Anspruch 5 oder 6, wobei der geschäumte poröse Nickelkörper und der faserartige poröse Nickelkörper ein Flächengewicht von 200 bis 700 g/m² besitzen.
8. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach einem der vorstehenden Ansprüche, wobei das aktive Material mindestens eines enthält, das aus der Gruppe ausgewählt ist, welche aus Verbindungen von Yttrium, Indium, Antimon, Barium und Beryllium besteht.
9. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach Anspruch 8, wobei die Verbindungen von Yttrium, Indium, Antimon, Barium und Beryllium Y_2O_3 , $Y(OH)_3$, In_2O_3 , In_2O , $In_2O_3 \cdot H_2O$, Sb_2O_3 , Sb_2O_4 , $Ba(OH)_2$, BeO und $Be(OH)_2$ sind.
10. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach Anspruch 8 oder 9, wobei die Verbindungen von Yttrium, Indium, Antimon, Barium und Beryllium in einer Menge von 0,5 bis 5 Gewichtsteilen auf 100 Gewichtsteile des Nickeloxids enthalten sind.
11. Positive Nickelektrode zur Verwendung in alkalischen Speicherbatterien nach einem der vorstehenden Ansprüche, wobei das Nickeloxid wie sphärische Nickelhydroxidpartikel ist.
12. Alkalische Speicherbatterie, die eine positive Nickelektrode nach einem der vorstehenden Ansprüche enthält.
13. Nickel-Wasserstoff Speicherbatterie, welche eine positive Nickelektrode aufweist, aufweisend ein aktives Material welches einen Hauptbestandteil aus Nickeloxid, eine negative Elektrode, die aus einem Hauptkörper besteht, der aus einer Wasserstoffspeicher-Legierung aufgebaut ist, die in der Lage ist, Wasserstoff elektrochemisch zu absorbieren und zu desorbieren, einen alkalischen Elektrolyten, einen Separator, ein Gehäuse, welches diese

Bestandteile umgibt, und eine mit einem Sicherheitsventil ausgerüstete Dichtplatte, wobei:

5 die positive Nickelelektrode vor dem anfänglichen Laden aufweist: Nickelhydroxid und Kobaltoxid, mindestens eines von Kobalt, Kobalthydroxid und Kobaltoxid, mindestens eines von Zinkoxid und Zinkhydroxid, und mindestens eine von Calciumverbindungen in einer Paste, wobei das mindestens eine von Zinkoxid und Zinkhydroxid 0,5 bis 5 Gewichtsteile beträgt, und die mindestens eine von Calciumverbindungen 0,5 bis 5 Gewichtsteile basierend auf 100 Gewichtsteilen des Nickeloxids beträgt;

10 einen voluminösen Körper, eine voluminöse poröse Platte oder eine voluminöse Platte, welche die Paste tragen und dieser eine elektrische Leitfähigkeit vermitteln;

15 wobei der alkalische Elektrolyt ein spezifisches Gewicht von 1,2 bis 1,3 bei 20°C besitzt;

die theoretische Kapazität der negativen Elektrode nicht weniger als das 1,1-fache der theoretischen Kapazität der positiven Elektrode beträgt; und

20 die Menge des Elektrolyten 1,0 bis 2,5 cm³/Ah Zellkapazität beträgt.

14. Nickel-Wasserstoff Speicherbatterie nach Anspruch 13, wobei die Calciumverbindung eine ist, die aus der Gruppe ausgewählt ist, welche aus Calciummoxid, Calciumhydroxid, Calciumfluorid, Calciumsulfid, Calciumperoxid und Calciumsilicat besteht.

25 15. Nickel-Wasserstoff Speicherbatterie nach Anspruch 13 oder 14, wobei der voluminöse poröse Körper einer ist, der aus der Gruppe ausgewählt ist, die aus einem geschäumten porösen Nickelkörper, einem faserartigen porösen Nickelkörper, einem gesinterten porösen Nickelkörper, einer porösen Platte, einem perforierten Metall und einem expandierten Metall besteht.

30 16. Nickel-Wasserstoff Speicherbatterie nach einem der Ansprüche 13 bis 15, wobei die Platte eine Nickelfolie oder eine nickelplattierte Eisenoxydfolie ist.

35 17. Nickel-Wasserstoff Speicherbatterie nach Anspruch 15 oder 16, wobei der geschäumte poröse Nickelkörper und der faserartige poröse Nickelkörper ein Flächengewicht von 200 bis 700 g/m² besitzen.

18. Nickel-Wasserstoff Speicherbatterie nach einem der Ansprüche 13 bis 17, wobei der alkalische Elektrolyt mindestens eines von Kaliumhydroxid und Natriumhydroxid, und Lithiumhydroxid enthält.

40 19. Nickel-Wasserstoff Speicherbatterie nach einem der Ansprüche 13 bis 18, wobei der Separator sulfoniert ist.

20. Nickel-Wasserstoff Speicherbatterie nach einem der Ansprüche 13 bis 19, wobei die positive Nickelelektrode mindestens eines enthält, das aus der Gruppe ausgewählt ist, welche aus Kohlenstoff und Nickel besteht.

Revendications

45 1. Électrode positive en nickel de type pâte pour l'utilisation dans des piles de stockage alcalines, comprenant une matière active contenant un constituant majeur d'oxyde de nickel et un support choisi dans le groupe constitué d'un corps poreux en volume, d'une plaque poreuse et d'une plaque supportant ladite matière active et lui conférant de l'électroconductivité, dans laquelle ladite matière active contient au moins un ingrédient choisi dans le groupe constitué du cobalt, de l'hydroxyde de cobalt et de l'oxyde de cobalt, au moins l'un des composés du calcium et au moins un composé choisi dans le groupe constitué de l'oxyde de zinc et de l'hydroxyde de zinc, ledit composé du calcium et ledit composé du zinc étant chacun inclus en une proportion de 0,5 à 5 parties en poids sur la base de 100 parties en poids dudit oxyde de nickel.

50 2. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon la revendication 1, dans laquelle ledit composé du calcium est choisi dans le groupe constitué de l'oxyde de calcium, de l'hydroxyde de calcium, du fluorure de calcium, du sulfure de calcium, du peroxyde de calcium et du silicate de calcium.

55 3. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon la revendication 1 ou 2,

dans laquelle ladite matière active est de type pâte.

4. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon la revendication 3, dans laquelle ladite matière active contient au moins un élément choisi dans le groupe constitué du carbone et du nickel.
5. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon l'une quelconque des revendications précédentes, dans laquelle ledit corps poreux en volume est un composé choisi dans le groupe constitué d'un corps en nickel poreux expansé, d'un corps en nickel poreux fibreux, d'un corps en nickel poreux fritté, d'une plaque poreuse, d'un métal perforé et d'un métal expansé.
10. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon l'une quelconque des revendications précédentes, dans laquelle ladite plaque est une feuille de nickel ou de fer plaquée de nickel.
15. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon la revendication 5 ou 6, dans laquelle ledit corps en nickel poreux expansé et ledit corps en nickel poreux fibreux ont un poids de 200 à 700 g/m².
20. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon l'une quelconque des revendications précédentes, dans laquelle ladite matière active contient au moins un composé choisi dans le groupe constitué des composés de l'yttrium, de l'indium, de l'antimoine, du baryum et du béryllium.
25. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon la revendication 8 dans laquelle lesdits composés d'yttrium, d'indium, d'antimoine, de baryum et de béryllium sont Y₂O₃, Y(OH)₃, In₂O₃, In₂O₃.H₂O, Sb₂O₃, Sb₂O₄, Ba(OH)₂, BeO et Be(OH)₂.
30. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon la revendication 8 ou 9, dans laquelle lesdits composés d'yttrium, d'indium, d'antimoine, de baryum et de béryllium sont inclus en une proportion de 0,5 à 5 parties en poids sur la base de 100 parties en poids dudit oxyde de nickel.
35. Électrode positive en nickel pour l'utilisation dans des piles de stockage alcalines selon l'une quelconque des revendications précédentes, dans laquelle ledit oxyde de nickel est en particules d'hydroxyde de nickel quasi-sphériques.
40. Pile de stockage alcaline contenant une électrode positive en nickel selon l'une quelconque des revendications précédentes :
45. • ladite électrode positive en nickel, avant de la charge initiale, comprend de l'hydroxyde de nickel, au moins un ingrédient parmi le cobalt, l'hydroxyde de cobalt et l'oxyde de cobalt, au moins un composé parmi l'oxyde de zinc et l'hydroxyde de zinc et au moins l'un des composés du calcium dans une pâte, ledit au moins un composé choisi parmi l'oxyde de zinc et l'hydroxyde de zinc représentant 0,5 à 5 parties en poids, ledit au moins un des composés du calcium représentant 0,5 à 5 parties en poids, sur la base de 100 parties en poids de l'hydroxyde de nickel ;
50. • un corps poreux en volume, une plaque poreuse, ou une plaque supportant ladite pâte et lui conférant de l'électro-conductivité ;
- ledit électrolyte alcalin ayant une densité de 1,2 à 1,3 à 20°C
- la capacité théorique de l'électrode négative n'étant pas inférieure à 1,1 fois la capacité théorique de l'électrode positive ; et
- la quantité d'électrolyte étant 1,0 à 2,5 cm³/Ah de capacité de la pile.
55. 14. Pile de stockage nickel-hydrogène selon la revendication 13, dans laquelle ledit composé du calcium est un composé choisi dans le groupe constitué de l'oxyde de calcium, de l'hydroxyde de calcium, du fluorure de calcium, du sulfure de calcium, du peroxyde de calcium et du silicate de calcium.

15. Pile de stockage nickel-hydrogène selon la revendication 13 ou 14, dans laquelle ledit corps poreux en volume est un corps choisi dans le groupe constitué d'un corps en nickel poreux expansé d'un corps en nickel poreux fibreux, d'un corps en nickel poreux fritté, d'une plaque poreuse, d'un métal perforé et d'un métal expansé.

5 16. Pile de stockage nickel-hydrogène selon l'une quelconque des revendications 13 à 15, dans laquelle ladite plaque est une feuille de nickel ou de fer plaquée de nickel.

17. Pile de stockage nickel-hydrogène selon la revendication 15 ou 16, dans laquelle ledit corps en nickel poreux expansé et ledit corps en nickel poreux fibreux ont un poids de 200 à 700 g/m².

10 18. Pile de stockage nickel-hydrogène selon l'une quelconque des revendications 13 à 17, dans laquelle ledit électrolyte alcalin comprend au moins un composé parmi l'hydroxyde de potassium et l'hydroxyde de sodium, et de l'hydroxyde de lithium.

15 19. Pile de stockage nickel-hydrogène selon l'une quelconque des revendications 13 à 18, dans laquelle ledit séparateur est sulfoné.

20 20. Pile de stockage nickel-hydrogène selon l'une quelconque des revendications 13 à 19, dans laquelle ladite électrode positive en nickel contient au moins un élément choisi dans le groupe constitué du carbone et du nickel.

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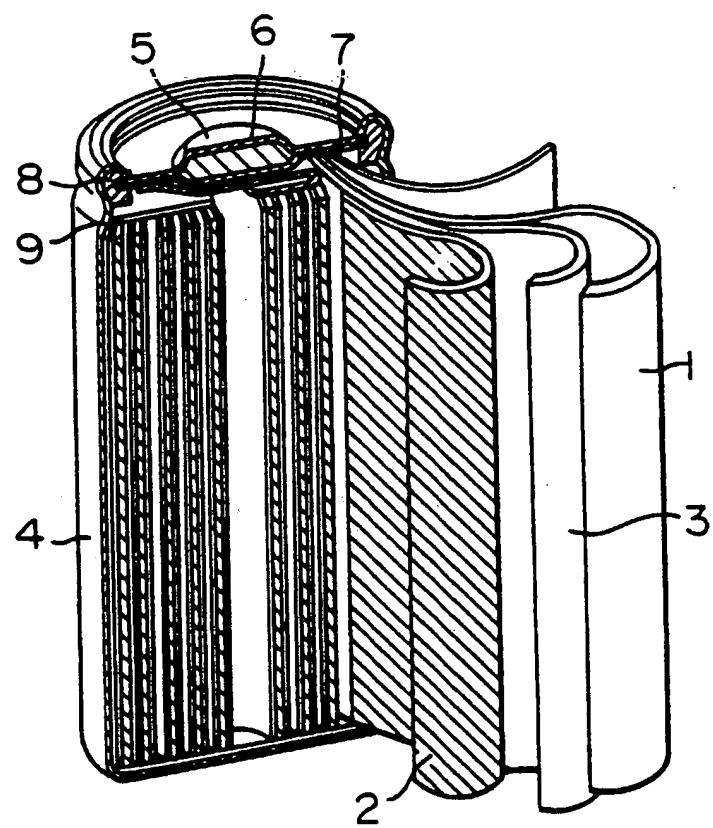
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FIG. 1



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